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(71) Applicant: AMERICAN INK JET CORPORATION [US/US]; 13 Alexander Road, Billerica, MA 01821-9956 (US).

(72) Inventors: DOLL, Paul, F.; Apartment E-4, 117 Central Street, Acton, MA 01720 (US). KELLY, Sean, M.; 8 Ransom Road, Framingham, MA 01701 (US).

(74) Agents: ARNOLD, Beth, E. et al.; Foley, Hoag & Eliot LLP, One Post Office Square, Boston, MA 02109 (US).

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(54) Title: WATERFAST PIGMENTED INK JET INKS

(57) Abstract

The ink composition as described herein for ink jet printers of thermal, piezoelectric, and continuous technologies comprises an aqueous vehicle, a negatively charged colloid pigment to prevent settling of the pigment, and polyamidoamine dendrimer to promote waterfastness. Optional additives to the ink formula may be suitable humectants, surfactants, and biocides. These inks exhibit good uncap times, good storage stability, and also yield prints with excellent quality.

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WATERFAST PIGMENTED INK JET INKS

Cross-Reference to Related Applications

This application is based upon United States Provisional Patent Application Number 60/021,967, filed June 27, 1996.

Background of The Invention

1. Field of the Invention

This application relates to the field of inks and more particularly to the field of inks for ink jet printers.

2. Description of Related Art

Ink jet printing is a non-impact method in which in response to a digitally produced signal, a drop of ink is ejected form a small orifice onto a substrate. Each drop produces one picture element (pixel) of the printed image. These small orifices being only 10 to 60 micrometers in diameter are very susceptible to clogging, which destroys the functionality of the entire printer. If the ink is not completely stable, either flocculation of colorant will occur or due to evaporation of the aqueous carrier at the jet orifices, or the colorant will precipitate out and clog the jets.

The issue of latency is very important to having a practical ink jet printer. An operator will want his printer to immediately work correctly even if he hasn't printed anything in weeks or months. The original field of aqueous ink jet inks dealt solely

with the art of dyes to provide colorants to the inks because many dyes of high purity that are thermally stable yield stable solutions that do not clog the ink jet orifices; however, most current dyes have low densities (because the colorant penetrates into the media), poor waterfastness, and poor lightfastness. Dye-based inks typicaly have an aqueous carrier. The aqueous carrier can move, or migrate, upon application of the ink to a printing medium, such as paper.

In contrast to dyes, pigments give desired image qualities because they are larger insoluble particles and once they are on the receiving media they do not migrate with the ink's aqueous carrier; thus, tighter crisper dots can be formed. This allows for crisper higher contrast edges on printed images than is typical for dye-based inks. Since the pigment does not migrate on or in the media, image quality will not vary from one quality of media to the next. Also, pigments, being larger particles, are typically more opaque and denser than dyes. While these qualities may not always be wanted for colored inks, these qualities promote high quality black ink image qualities.

Typically pigments are held in aqueous suspension with the aid of surfactants, polymers, or polyelectrolytes. These pigmented inks may also be formulated with binders which adhere the pigment to the substrate and improve the waterfastness of the print. However, these pigment dispersions have high viscosities and low surface tensions while ink jet inks typically have low viscosities and high surface tensions.

Cabot Corporation has recently disclosed a carbon black pigment made for aqueous ink jet printing. The carbon black is a negatively charged colloid which can yield inks with low viscosities and high surface tensions, giving ink formulators flexibility they didn't previously have. However since no resin is in the system, prints made with the Cabot pigment have no waterfastness. Thus, when the inks or the printing media are exposed to water, the inks run, destroying image quality.

There is a need to find a binder that will make carbon black, pigmented inks, such as the Cabot carbon black ink, waterfast, while not affecting the stability of the negatively charge colloid.

A relatively new area in polymer chemistry was started by Dow Chemical when they synthesized precise macromolecules by nonbiological methods. These dendritic polymers have since been found to have many desired characteristics, since their synthesis is completely controlled, allowing the custom designing of polymers. The synthesis of these globular dendrimers consists of growing well-defined branches from a central core in successive steps. A detailed description of the radial type dendrimers and their synthesis can be found in US Patent 5,338,532 to Tomalia et al.

Summary Of The Invention

The present invention provides an aqueous, pigmented ink jet ink composition with low viscosity, high surface tension, waterfastness, and good latency.

Detailed Description of the Preferred Embodiment(s)

In an embodiment of the present invention, a micro-dispersion of Cabot CSX 440 carbon black pigment with typical particle size range 0,02 - 2.00 micrometers, preferably 0.02 - 1.20 is mixed with water. Best results are achieved when water is purified through reverse osmosis, and/or de-ionization, and/or distillation, as this assures no contamination from unknown chemicals. Typically, the concentration of the percent solids of the Cabot CSX-440 used is 2% to 10%, or preferably from 3% to 7%, based on total weight of the ink. Concentrations greater than these do not increase print density, but do increase the likelihood of pigment flocculation while concentrations less than these do not provide for suitable densities.

In an embodiment of the invention, a biocide is added to the ink to extend its shelf life. Any of the following biocides have been found to be suitable: Proxel GXL (Zeneca, Wilmington, DE), Proxel XL2 (Zeneca, Wilmington, DE), Dowacides (Dow Chemical, Midland, MI).

In an embodiment of the invention, the final ink formulation is filtered down to less than 5.0 micrometers, preferably less than 2.0 micrometers to ensure that there are no particles in the ink large enough to clog a jet orifice. Thus, if a jet does clog it must be due to flocculation of the pigment.

Also, the addition of a surface acting agent (surfactant) to this ink may be used to enhance the wetting ability of the ink and improve this invention's dry time and printing characteristics. Surfactants are generally used in very low percentages, typically 0.001% to 1.000% to achieve surface tensions in the range of 30 to 65 dynes/cm. Anionic, cationic, or non-ionic surfactants may be used in this invention, preferably non-ionic because these are less likely to destabilize the negatively charged colloid pigment.

In an embodiment of the invention a humectant is added to the ink to keep the jet orifices from clogging when the water carrier starts to evaporate. These water soluble organic solvents may be used in weight percentages from 0.5% to 50% as well as being used in varying combinations. Representative examples of water soluble organic solvents that may be used with this invention are polyhydric alcohols, such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, and thiodiglycol; and nitrogen-containing cyclic compounds such as 2-pyrrolidinone, and N-methyl-2-pyrrolidinone. The following examples show that polyethylene glycol (w Avg. molecular weight 200), and 2-pyrrolidinone and preferably 2-pyrrolidinone, exhibit the best anti-clogging properties.

Example 1: To 87.8 grams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 6.0 grams of diethylene glycol were added, and these components were then mixed to evenly distribute them through the solution. Then 6.0 grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then

filtered down through a 0.22 micron filter.

Example 2: To 87.8 grams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 6.0 grams of glycerol were added, and these components were then mixed to evenly distribute them through the solution. Then 6.0 grams of Cabot CSX 440 E was added and then further mixed for 15 minutes. This ink was then filtered down through a 0.22 micron filter.

Example 3: To 87.8 grams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 6.0 grams of triethylene glycol were added, and these components were then mixed to evenly distribute them through the solution. Then 6.0 grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then filtered down through a 0.22 micron filter.

Example 4: To 87.8 grams of purified water, 0.2 &rams of Proxel G.X.L. were added. Further, 6.0 grams of 2-pyrrolidinone were added, and these components were then mixed to evenly distribute them through the solution. Then 6.0 grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then filtered down through a 0.22 micron filter.

Example 5: To 87.8 grams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 6.0 grams of polyethylene glycol (200) were added, and these components were then mixed to evenly distribute them through the solution. Then 6.0

grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then filtered down through a 0.22 micron filter.

In an embodiment of the invention, an accelerated latency test can be performed by leaving an ink jet cartridge full of the ink to be tested outside of its normal resting housing that caps the jets to reduce evaporation and increase cartridge latency. Uncap times for the preceding examples were then determined by filling clean and empty ink jet cartridge with an ink to be tested; then a test pattern that uses and identifies all 50 of the nozzles was printed and recorded; then the cartridge was removed from the printer and placed in an uncapped position for a determined period of time; then the cartridge was placed back into the printer and the test pattern was printed again to determine if any jets had clogged and to what extent (how many); then the cartridge was again removed and left uncapped for a longer period of time before being checked again by printing a test pattern. This process is repeated over and over until the cartridge has a clog or an uncap time of one week (168 hours) has been achieved.

Number of Clogged Jets

Uncapped Time	Example 1	Example 2	Example 3	Example 4	Example 5
5 min.	NA	0	10	0	0
10 min.	23	0	------	0	0
15 min.	------	2	------	0	0
20 min.	------	18	------	0	1

30 min.	------	------	------	0	1
90 min.	------	------	------	0	1
120 min.	------	------	------	0	3
24 hours	------	------	------	0	------
168 hours	------	------	------	0	------

This base formulation can be further modified by adding a dendritic polymer to improve the water resistance of this ink and preferably a radial dendrimer and more preferably a STARBURST PAMAM (polyamidoamine) dendrimer dendrimer (DENDRITECH, Inc., Midland, NE), and still more preferably a STARBURST PAMAM (polyamidoamine) dendrimer of the 1" generation.

The number of surface groups of a STARBURST PAMAM double with each generation. And with each generation the molecular weight of the dendrimer more than doubles.

GENERATION	MOLECULAR WEIGHT	MEASURED DIAMETER	SURFACE GROUPS
1	1,430	22A	8
2	3,256	29A	16
3	6,909	36 A	32

Thus, the larger dendrimer molecules crosslink enough pigment particles to destabilize the negatively charged colloid. The following examples show that the pigmented ink of this invention can be made equally waterfast with a lower generation STARBURST PAMAM dendrimer by roughly doubling the weight percentage used in

the from the next higher generation STARBURST PAMAM dendrimer: and that these lower generation dendrimers while exhibiting equal or better waterfastness yield better cartridge latency times.

Example 1: To 69.6 grams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 18.0 grams of polyethylene glycol (200) were added, further 0.1 grams of Surfynol 465 (Air Products and Chemicals, Inc., Allentown, PA) was added, further 0.1 grams of STARBURST PAMAM dendrimer (3,d generation) were added, and then these components were mixed to evenly distribute them throughout the solution. Then 12.0 grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then filtered down through a filter ladder to a final filter size of 0.22 microns. Eight 47mm mixed cellulose 0.22 micron filters were required to filter all 100 grams.

Example 2: To 69.5 gams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 18.0 grams of polyethylene glycol (200) were added, further 0.1 grams of Surfynol 465 was added, further 0.2 grams of STARBURST PAMAM dendrimer (2nd generation) were added, and then these components were mixed to evenly distribute them throughout the solution. Then 12.0 grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then filtered down through a filter ladder to a final filter size of 0.22 microns. Upon which all 100 grams passed through a single 47mm mixed cellulose 0.22 micron filter.

Example 3: To 69.2 grams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 18.0 grams of polyethylene glycol (200) were added, further 0. I grams of Surfynol 465 was added, further 0.5 grams of STARBURST PAMAM dendrimer (I" generation) were added, and then these components were mixed to evenly distribute them throughout the solution. Then 12.0 grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then filtered down through a filter ladder to a final filter size of 0.22 microns. Upon which all 100 grams passed through a single 47mm mixed cellulose 0.22 micron filter.

Example 4: To 64.8 grams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 18.5 grams of polyethylene glycol (200) were added, further 0.1 grams of tetraethylene pentamine were added, and then these components were mixed to evenly distribute them throughout the solution. Then 16.0 grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then filtered down through a filter ladder to a final filter size of 0.22 microns. Upon which all 100 grams passed through a single 47mm mixed cellulose 0.22 micron filter.

Example 5: To 64.8 gams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 18.5 grams of polyethylene glycol (200) were added, further 0.1 grams of a polyamide amine resin (Cartaretin F-4 Liquid, Clariant Corporation, Charlotte, NC) were added, and then these components were mixed to evenly distribute them throughout the solution. Then 16.0 grams of Cabot CSX 440 was added and then further mixed for 15 minutes. This ink was then filtered down through a filter ladder

to a final filter size of 0.22 microns. Much pigment was being filtered out and ten 47mm mixed cellulose 0.22 micron filters used just to obtain 15 grams of ink for testing purposes.

Example 6: To 87.3 grams of purified water, 0.2 grams of Proxel G.X.L. were added. Further, 10.0 grams of polyethylene glycol (200) were added, further 0.5 grams of STARBURST PAMAM dendrimer (2- generation) were added, and then these components were mixed to evenly distribute them throughout the solution. Then 2.0 grams of FD&C Blue #1 was added to the mixture and stirred magnetically for 15 minutes. All 100 grams passed through a single 47mm mixed cellulose 0.22 micron filter.

	Latency	**Filterability**	**Waterfastness**
Example 1	**poor**	**poor**	**good**
Example 2	**fair**	**good**	**good**
Example 3	**good**	**good**	**good**
Example 4	**NA**	**good**	**poor**
Example 5	**NA**	**poor**	**poor**
Example 6	**NA**	**excellent**	**poor**

Examples 1, 2, and 3 support the claim that a generation of dendrimers exhibit equal waterfastness and better latency than the next higher generation of dendrimers when the lower generation dendrimer is used in a percentage of the total weight percentage of the ink that is roughly twice that used with the higher generation dendrimer.

Examples 4, 5, and 6 support the uniqueness of this invention. Examples 4 and 5 show the inability of other poly amines to promote waterfastness in this pigmented ink system. And Example 6 shows the inability of the STARBURST PAMAM dendrimer to promote waterfastness in other ink systems.

While the invention has been disclosed in connection with the preferred embodiments shown and described in detail, various modifications and improvements thereon will become readily apparent to those skilled in the art. Accordingly, the spirit and scope of the present invention is to be limited only by the following claims.

Claim(s)

What is claimed is:

1. A pigmented ink for use in ink jet printers, comprising:

purified water,

a biocide,

a humectant, and

a predispersed negatively charged colloid pigment.

2. The pigmented ink of claim 1, wherein the colloid pigment is Cabot predispersed negatively charged carbon black colloid.

3. The pigmented ink of claim 2, wherein the colloid pigment is Cabot CSX 440.

4. The ink of wherein the biocide is present in a weight percentage amount from 0.01% to 1.00%.

5. The ink of claim 1 wherein the humectant is selected from the group consisting of polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, and thiodiglycol and nitrogen containing cyclic compounds such as 2-pyrrolidinone, and N-methyl-2-pyrrolidinone.

6. The ink of claim 5, wherein the humectants are used individually or in

combination in weight percentages from 0.1% to 80%, and preferably 1.0% to 40/o, and more preferably 1.0% to 20%.

7. An ink in accordance with claim 1 further comprising a surfactant.

8. The ink of claim 7, wherein the surfactant is cationic, anionic, or nonionic.

8. The ink of claim 7, wherein the surfactant is non-ionic.

9. The ink of claim 8, wherein the surfactant is used in weight percentages from 0.001% to 1.000%.

10. The ink of claim 1, further comprising a dendrimer.

11. The ink of claim 10, wherein the dendrimer is a first, second, or third generation dendrimer.

12. The ink of claim 10, wherein the dendrimer is a STARBURST PAMAM dendrimer.

13. The ink of claim 12, wherein the dendrimer is a first generation STARBURST PAMAM dendrimer.

14. A pigmented ink for use in ink jet printers, comprising:

purified water;

a biocide;

a humectant;

a surfactant;

a predispersed negatively charged colloid pigment; and

a dendrimer.

15. The ink of claim 14, wherein the dendrimer is a STARBURST PAMAM dendrimer.

16. The ink of claim 14 wherein the surfactant is nonionic and is used in weight percentages from 0.001% to 1.000%.

17. The ink of claim 14 wherein the humectant is selected from the group consisting of polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, and thiodiglycol and nitrogen containing cyclic compounds such as 2-pyrrolidinone, and N-methyl-2-pyrrolidinone.

18. The ink of claim 14, wherein the colloid pigment is Cabot predispersed negatively charged carbon black colloid.

19. The ink of claim 14, wherein the biocide is present in a weight percentage amount from 0.01% to 1.00%.

20. A pigmented ink for use in ink jet printers, comprising:

purified water;

a biocide, wherein the biocide is present in a weight percentage amount from 0.01% to 1.00%;

a humectant, wherein the humectant is selected from the group consisting of polyhydric alcohols such as ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, tetraethylene glycol, polyethylene glycol, glycerol, and thiodiglycol and nitrogen containing cyclic compounds such as 2-pyrrolidinone, and N-methyl-2-pyrrolidinone;

a surfactant, wherein the surfactant is nonionic and is used in weight percentages from 0.001% to 1.000%;

a predispersed negatively charged colloid pigment, wherein the colloid pigment is Cabot predispersed negatively charged carbon black colloid; and

a dendrimer, wherein the dendrimer is a STARBURST PAMAM dendrimer.

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INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C09D11/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 718 383 A (XEROX CORPORATION) 26 June 1996 see abstract see page 3, line 28-32 see page 4, line 57 - page 5, line 8 see page 5, line 38-46 see page 6, line 2-19; example II ---	1,2,4-9
X	EP 0 475 075 A (XEROX CORPORATION) 18 March 1992 see page 4, line 40 - page 5, line 36 see page 6, line 17-19 see page 6, line 53-54 see page 8, paragraph 2-4 --- -/--	1,2,4-9

[X] Further documents are listed in the continuation of box C.

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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Girard, Y

INTERNATIONAL SEARCH REPORT

Inte. onal Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 5 596 027 A (SHARON B. MEAD) 21 January 1997 see abstract see column 6, line 22-62 see column 9, line 4-10 see column 12, line 53-62 see column 13, paragraph 1 see column 13, paragraph 5-6 ---	1-20
A	US 5 120 361 A (FRANCOISE M. WINNIK) 9 June 1992 -----	1,14

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. ional Application No
PCT/US 97/11571

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 718383 A	26-06-96	US 5531818 A	02-07-96
EP 475075 A	18-03-92	US 5281261 A	25-01-94
		CA 2046571 A,C	01-03-92
		DE 69114962 D	11-01-96
		DE 69114962 T	18-04-96
		JP 4234467 A	24-08-92
US 5596027 A	21-01-97	AU 6310296 A	10-02-97
		WO 9703137 A	30-01-97
US 5120361 A	09-06-92	NONE	

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